

## REMARKS

Claims 1-20 are pending in this application. The Examiner has maintained the rejection of:

- (1) claim 1 under 35 U.S.C. § 102(b) over Herman, *Global Cosmetic Industry*, vol. 162, no. 2, pp. 22-24 ("*Herman*" reference);
- (2) claims 2-3, 10-17 and 20 under 35 U.S.C. § 103(a) over Herman in view of US-A-6,046,145 ("*Santora*" reference);
- (3) claims 4-9 under 35 U.S.C. § 103(a) over Herman and Santora in view of US-A-4,940,577 ("*Greenberg*" reference); and
- (4) claims 18-19 under 35 U.S.C. § 103(a) over Herman in view of US-A-5,256,396 ("*Piechota*" reference).

Applicants are herein cancelling claims 18-19, without prejudice, leaving claims 1-17 and 20 upon entry of this amendment.

Applicants submit that the amendment to the claims does not introduce new matter and is fully supported by the specification and claims, as originally filed. Applicants request the Examiner to enter the amendment under 37 C.F.R. § 1.116(b) because the amendments to the claims either cancel claims, comply with requirements of form expressly set forth in a previous Office Action, or present the rejected claims in better form for consideration on appeal.

Rejection under 35 U.S.C. § 102(b) over Herman

The Examiner has maintained the rejection of claim 1 under 35 U.S.C. § 102(b) over Herman, *Global Cosmetic Industry*, vol. 162, no. 2, pp. 22-24 ("*Herman*" reference). Applicants respectfully traverse because the Herman reference does not disclose each and every element of applicants' claimed method, as defined by claim 1, and thus does not anticipate claim 1 under 35 U.S.C. § 102(b).

Specifically, Herman does not disclose a ringing gel composition containing a benefit agent, as defined by applicants on page 4, lines 10-12. The Examiner alleges that carbomers

are equivalent to the film-forming agents set forth in the specification on page 12, line 12 in the list of benefit agents that may be delivered via the method of the invention. Applicants submit that carbomers are not film-forming agents. Carbomers are high molecular weight polymers of acrylic acid backbones with small amounts of polyalkenyl polyether crosslinking agents. They are brittle when dry and do not form films. As evidence, please see Noveon brochure; Desai *et al.* "Advances in Carbomer Polymer Technology" brochure from BFGoodrich; and excerpt from Billymeyer, *Textbook of Polymer Science*, (New York: John Wiley & Sons, 1984), pages 389-390.

Because carbomers are not film-forming agents, the *Herman* reference does not disclose each and every element of claim 1, as required for anticipation. Accordingly, applicants request the Examiner to withdraw the rejection of claim 1 under 35 U.S.C. § 102(b) as anticipated by *Herman*.

**Rejection under 35 U.S.C. § 103(a) over *Herman* in view of *Santora***

The Examiner has maintained the rejection of claims 2-3, 10-17 and 20 under 35 U.S.C. § 103(a) over *Herman* in view of US-A-6,046,145 ("*Santora*" reference) alleging that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have modified the composition of *Herman* to add the specific surfactants and cosmetic actives of *Santora* to reach applicants' claimed invention, as defined by claims 2-3, 10-17 and 20. Applicants respectfully traverse because the Examiner has failed to show that the references are properly combinable to establish a *prima facie* case of obviousness.

As discussed above with respect to claim 1, *Herman* does not disclose, teach or suggest a ringing gel composition containing any benefit agent. *Santora* is wholly silent with respect to ringing gels in general and to their use in a method to deposit benefit agents to keratinous surfaces. While *Herman* does mention the use of ringing gels in upscale skin care applications, he urges that the reason the ringing gels are used is because they make products into which they are incorporated "attractive" in terms of feel (in ethnic hair care applications, for example) and "clarity" (in fragrance applications, for example). *Herman* does not disclose, teach or suggest using ringing gel compositions to deliver any benefit agent, especially compositions that will not only cleanse but also leave a particular benefit agent

behind, even after rinsing the composition off of the hair, skin or nails. *Santora* does not remedy this deficiency. .

5 It is applicants who have discovered the use of the ringing gel compositions to deliver benefit agents to the hair, skin and nails. Applicants submit that the Examiner is improperly engaging hindsight to reconstruct applicants' claimed invention by picking and choosing among the references without motivation to do so or any reasonable expectation of success. As such, applicants submit that the Examiner has failed to establish a *prima facie* case of obviousness.

10 Because *Santora* does not remedy the deficiencies of *Herman*, applicants submit that the Examiner has not established a case of *prima facie* obviousness and the Examiner to withdraw the rejection of claims 2-3, 10-17 and 20 under 35 U.S.C. § 103(a).

15 **Rejection under 35 U.S.C. § 103(a) over *Herman* and *Santora* in view of *Greenberg***

The Examiner has maintained the rejection of claims 4-9 under 35 U.S.C. § 103(a) over *Herman* and *Santora* in view of US-A-4,940,577 ("*Greenberg*" reference); alleging that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have modified the composition of *Herman* to add the specific surfactants and cosmetic actives of *Santora* at the levels disclosed by *Greenberg* to reach applicants' claimed invention, as defined by claims 4-9. Applicants respectfully traverse because the Examiner has failed to show that the references are properly combinable to establish a *prima facie* case of obviousness.

25 As discussed above with respect to claim 1, *Herman* does not disclose, teach or suggest a ringing gel composition containing any benefit agent. *Santora* is wholly silent with respect to ringing gels in general and to their use in a method to deposit benefit agents to keratinous surfaces. While *Herman* does mention the use of ringing gels in upscale skin care applications, he urges that the reason the ringing gels are used is because they make products into which they are incorporated "attractive" in terms of feel (in ethnic hair care applications, for example) and "clarity" (in fragrance applications, for example). *Herman* does not disclose, teach or suggest using ringing gel compositions to deliver any benefit agent,

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especially compositions that will not only cleanse but also leave a particular benefit agent behind, even after rinsing the composition off of the hair, skin or nails. Neither *Santora* or *Greenberg* or both remedy this deficiency. .

5           It is applicants who have discovered the use of the ringing gel compositions to deliver benefit agents to the hair, skin and nails. Applicants submit that the Examiner is improperly engaging hindsight to reconstruct applicants' claimed invention by picking and choosing among the references without motivation to do so or any reasonable expectation of success. As such, applicants submit that the Examiner has failed to establish a *prima facie* case of  
10   obviousness.

          Because *Greenberg* also does not remedy the deficiencies in making the combination of *Herman* and *Santora*, applicants submit that the Examiner has not established a case of *prima facie* obviousness and the Examiner to withdraw the rejection of claims 4-9 under 35  
15   U.S.C. § 103(a).

**Rejection under 35 U.S.C. § 103(a) over *Herman* in view of *Piechota***

          The Examiner has maintained the rejection of claims 18-19 under 35 U.S.C. § 103(a)  
20   over *Herman* in view of US-A-5,256,396 ("*Piechota*" reference). Applicants are herein cancelling claims 18-19, without prejudice, thus rendering moot the rejection of claims 18-  
19.

Conclusions

Applicants request the Examiner to:

- 5 (1) enter the amendment cancelling claims 18-19; and  
(2) reconsider and withdraw the rejection of the remaining claims 1-17 and 20; and  
(3) pass claims 1-17 and 20 (as amended) to allowance.

If the Examiner is of a contrary view, the Examiner is requested to contact the undersigned attorney at (215) 557-3861.

10 Respectfully submitted,



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## Applications Technology for Carbopol<sup>®</sup> Resins and Cosmetic Formulations

Noveon, Inc. introduced Carbopol<sup>®</sup> 934 resin to the cosmetic industry in the middle 1950's. Since that time, a number of these products have been introduced. Those resins of most interest to the cosmetic chemist have been assigned the CTFA generic names of Carbomer 934, 940 and 941. These complementary products continue to meet the exacting ever-changing demands of advanced cosmetic products because of the properties Carbopol<sup>®</sup> resins provide.

**Safety:** A 25 year history demonstrating non-irritating, non-sensitizing use.

**Elegance:** Luxurious feel.

**Stability:** Assured shelf life and performance.

**Efficiency:** Effectiveness at very low concentrations.

**Microorganism Resistance:** No support for bacteria, mold, or fungus growth.

**Quality:** Assured, uniform performance.

**Versatility:** Performance across wide pH and viscosity ranges.

The aim of this paper is two-fold. The first is to provide a brief review of the fundamentals of Carbopol<sup>®</sup> resins technology. The second is the application of this technology to product formulation and production.

### Technology Overview

All the Carbopol<sup>®</sup> resins are dry, polyacrylic acid resins. When first dispersed in water or other solvent, they are tightly knotted together via hydrogen bonding. At normal use levels of up to 1% (Figure 1) no significant thickening occurs until the resins are partially neutralized with an appropriate base to form a salt. When this salt dissolves and ionizes, it swells into its most effective thickening form (Figure 2).

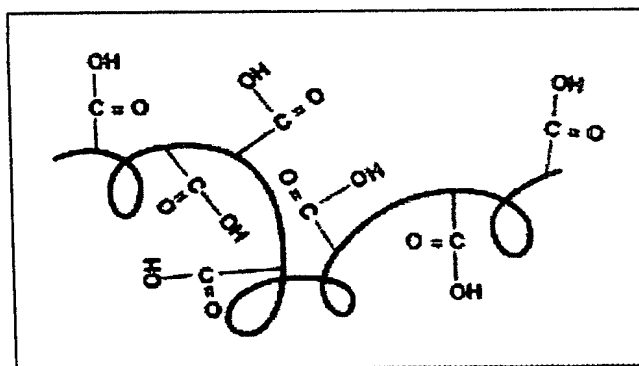
An electronic repulsion network gives the Carbopol<sup>®</sup> resins their efficiency (Figure 3). The Carbopol<sup>®</sup> resins are usually only partially neutralized since complete sodium hydroxide neutralization, for example, would produce a pH in excess of 10.

All of the Carbopol<sup>®</sup> resins operate via the same mechanism but each has its own attributes. Note, for example, the difference in viscosity development (Figure 4). Here, the resins have been neutralized to pH 7 with sodium hydroxide.

In addition, the optimum pH operating range varies somewhat with the Carbopol<sup>®</sup> resin (Figure 5). Note that with Carbopol<sup>®</sup> 940, the optimum pH operating range is from 3 to 11. Curves for the other Carbopol<sup>®</sup> resins are similar in shape but of different values.

A more appropriate description of Carbopol<sup>®</sup> resin performance would be as flow control agents. The reason for this is that once swollen, they generate

**Figure 1**  
**Schematic Depicting Molecule of Carbopol Resin in Relaxed State**



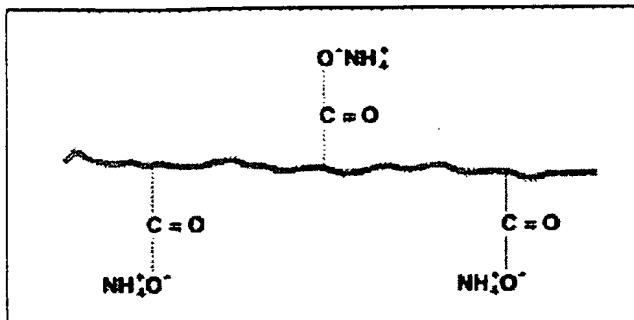
**CARBOPOL**  
**ETD** POLYMERS

**CARBOPOL**  
**Ultrez**  
POLYMER

**PEMULEN**  
POLYMERIC EMULSIFIERS

**AVALURE**  
FILM FORMING POLYMERS

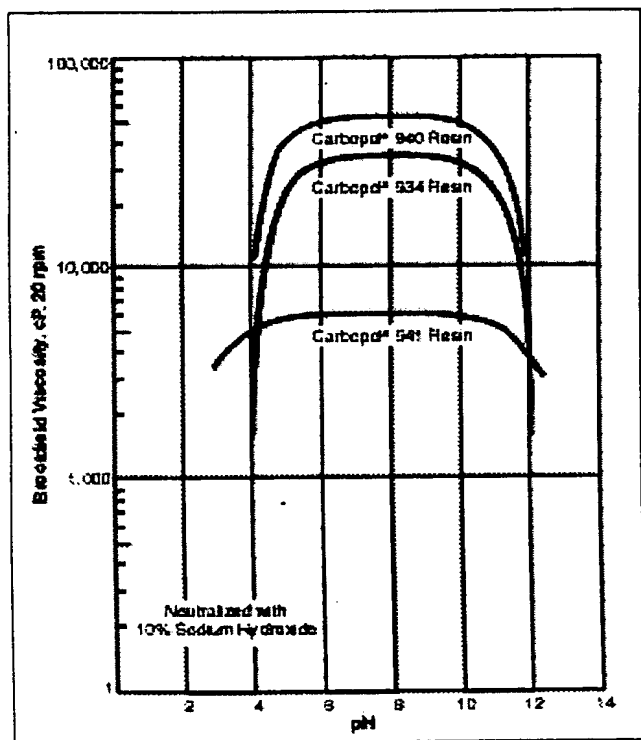
**Figure 2**  
Schematic Depicting Molecule of Carbopol Resin  
In Uncolled State



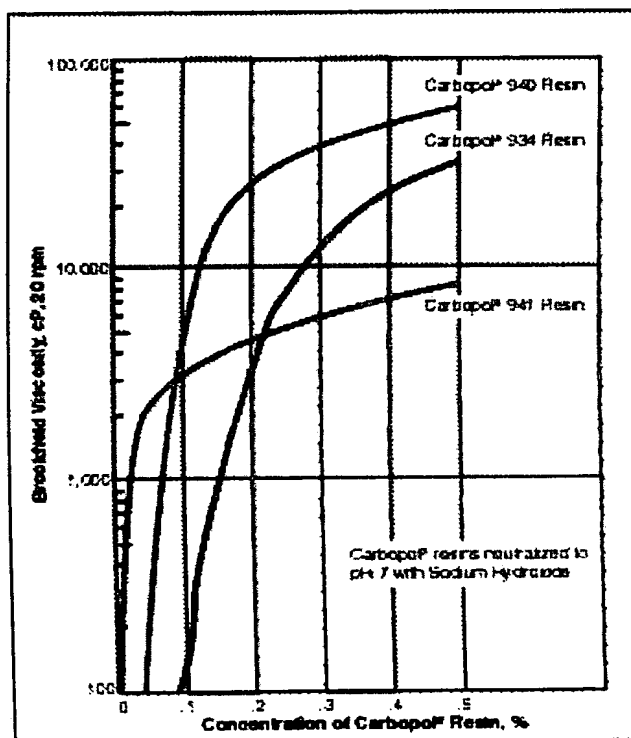
plastic flow systems and these systems exhibit the rheological property of Yield Value. Yield Value can be defined as an initial resistance to flow under applied stress. It is this property that elevates the Carbopol® resins above mere thickeners.

The importance of Yield Value in stabilizing emulsions and suspensions is that Yield Value is an opposing force to the gravitational movement of the dispersed phase and Yield Value accompanies viscosity generation with the Carbopol® resins. In addition to stabilizing emulsions and suspensions from separation, it provides freeze-thaw stability as well.

**Figure 3**  
Effect of pH on Viscosity of a 0.5% Solution  
of Carbopol Resin in Water



**Figure 4**  
Thickening Efficiency of Carbopol Resins at Low  
Concentrations in Water



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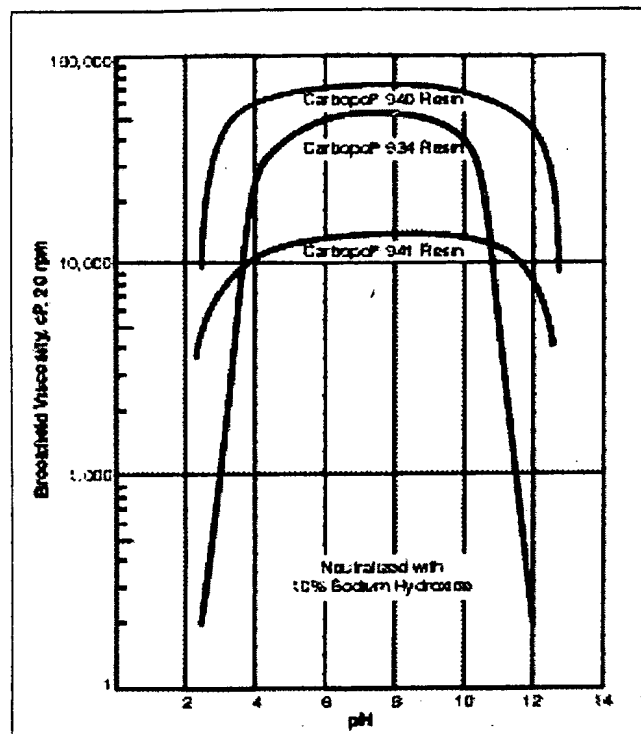
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**Figure 5**  
Effect of pH on Viscosity of a 1.0% Solution  
of Carbopol Resin in Water



An important point is that Yield Value imparts stability without the need for overwhelming viscosity. The gravitational pull on a suspended particle is directly proportional to the square of its diameter, (when the particles approach molecular size) the difference in specific gravities of the continuous and dispersed phases, and inversely proportional to the viscosity.

Selection of the proper Carbopol® resin is simplified by the following table.

### Selecting the Right Carbopol® Resin

Requirement	Recommended Carbopol® Resin
Clear gels > 3000 cP	940
Suspensions or emulsions at > 3000 cP	934, 940
Suspensions or emulsions at < 3000 cP	941
Higher shear resistance	934, 940
Better ion resistance	941
Better thermal stability	934, 940

\*Brookfield, 20 rpm, viscosities

### Neutralization

Having chosen a candidate resin, one then asks what neutralizing agent (base) to employ. Sodium or ammonium hydroxide, are useful as well as a variety of amines. Historically, alcoholic amines, such as triethanolamine, with low odor and color have been favored. Amines pose no threat of over-neutralization (with the subsequent viscosity loss) that is possible with alkali-metal hydroxides. Lower molecular weight amino acids, as neutralizing agents, form interesting Carbopol® resin salts due to their moisturizing contribution.

Recent concerns about nitrosamine-forming agents in cosmetics has stimulated a search for alternative neutralizing agents. Quadrol (BASF-Wyandotte) may be suitable. Quadrol is a very interesting neutralizing agent. It is useful in all-water or alcohol-water systems containing up to 50% alcohol. As with any material, one should contact the supplier concerning toxicological considerations.

Other valuable characteristics of these versatile Carbopol® resin products are often overlooked or poorly appreciated. Let's consider the whole Carbopol® resin character.

### Acidic Nature

The Carbopol® resins are polyacrylic acids. This means they are very hydrophilic. Secondly, the Carbopol® resins are anionic products that will normally react with any cations. The cations of neutralizing bases are well known to form a salt of the polymer. It is not always appreciated that cationic conditioning agents can also react with, and precipitate, the Carbopol® resins.

As acid products, just how acidic are the Carbopol® resins? The following table shows the ionization constants of several mild acids contrasted with that of Carbopol® 934:

Acid	Ionization Constant
Citric	75000 X 10 <sup>-7</sup>
Acetic	1800 X 10 <sup>-7</sup>
Carbonic	4.5 X 10 <sup>-7</sup>
Carbopol® 934	1.6 X 10 <sup>-7</sup>

If ionization constant is considered a reasonable measure of acid strength, then the Carbopol® resins are extremely mild. Nevertheless, they are active anions and will be sought by any cations in the system.



## Colloidal Nature

It is quite likely that each particle of Carbopol® resin is an individual molecule - a kind of three dimensional, hydrophilic network about 2 to 4 microns in diameter, i.e., super colloids. Many studies have confirmed that these swollen particles display a significant electrical charge, especially after neutralization, and attract each other. This particle to particle attraction explains Yield Value.

It is then easy to visualize the well-known shear recovery displayed by all the Carbopol® resin systems. The application of shear separates the particles, but they are rapidly snapped back together by electronic attraction upon shear release. For optimum Carbopol® resin service, consider the influence of any ingredients, such as salts or extraneous cations in the formula, that reduce this attraction, and hence, the Carbopol® resin's viscosity and Yield Value.

Looking at the total Carbopol® resin character then, one can assure success in employing these high-polymer, base-actuated, hydrophilic, colloidal, flow control agents.

## Technology Application

A company was producing a cream shampoo, thickened with Carbopol® 934, containing sodium lauryl sulfate (SLS). Suddenly, without a formulation or equipment change, the production viscosities went out of specification.

The problem? An aggressive buyer had purchased a cheaper grade of SLS containing a higher level of sodium sulfate. This ionic material was reducing the Carbopol® resin's swelling capability. To correct the problem was easy: return to the original SLS. A slight increase in Carbopol® resin level could also have solved the problem.

Frequently, order of addition, and/or choice of neutralizing agent, can avoid an interfering reaction. Water-based zinc oxide ointments have been successfully produced with Carbopol® resin products for years. However, care is necessary. A dispersion of zinc oxide, water, Carbopol® resin and sodium hydroxide quickly turns to a lumpy, cottage cheese consistency. Carbopol® resin will have its cation, and the zinc oxide offers a swamping concentration.

If one considers order of addition and neutralizer selection, success is possible. By first neutralizing the Carbopol® resin dispersion to a pH greater than

7.2 (with a strong base such as sodium hydroxide) and then adding the zinc oxide, a mixed, sodium-zinc half salt forms which results in a smooth, stable ointment.

But many times, an interaction expresses itself much more subtly.

## Hair Setting Gel

	<u>% By Weight</u>
PVP or protein film former	2
Water	q.s. 100
Triethanolamine	0.5
Carbopol® 940	0.5
Disodium EDTA	0.005
UV Absorber	0.005
Methyl paraben	0.1
Propyl paraben	0.1
Color	q.s.
Perfume	q.s.
Solubilizer	q.s.

If one neglects the fact that Carbopol® 940 is a high-polymer, acidic colloid, one is likely to disperse it with all the other ingredients in the water, and add the TEA as the last step. A smooth, stable gel will form if this is done.

However, polyvinylpyrrolidone (PVP) and protein film formers are somewhat cationic and flocculate the Carbopol® resins. This flocculation is reversed upon addition of the TEA, but gel clarity is frequently adversely affected.

To avoid this interaction, either neutralize the Carbopol® resin dispersion before addition of the PVP or protein or add the TEA combined with the PVP or protein.

Note in this formulation the use of Di-sodium EDTA and a UV absorber. Unprotected, clear, Carbopol® resin gels, packaged in clear containers and exposed to light, gradually lose viscosity; and the loss is permanent. Generally, this can be effectively inhibited with the use of one percent Di-sodium EDTA plus one percent UV absorber, with both percentages based on the weight of the Carbopol® resin present. This stabilization is normally unnecessary in Carbopol® resin products such as creams and lotions.

## Sparkling Sunscreen Lotion

This formulation can be easily handled because there is no significant interaction of the actives with the Carbopol<sup>®</sup> resin and the ethanol offers simple addition.

## Sparkling Clear Sunscreen Lotion

<u>Ingredients</u>	<u>Parts</u>
Ethanol	16.0
H <sub>2</sub> O	50.0
Carbopol <sup>®</sup> 941	1.0
Arlamol E <sup>(1)</sup>	20.0
Amerscreen P <sup>(2)</sup>	10.0
Brij-98 <sup>(3)</sup>	1.0
Quadrol <sup>(4)</sup> (50% water solution)	2.0
Brookfield Viscosity, cps	2,630

<sup>(1)</sup> Arlamol E ICI America

<sup>(2)</sup> Amerscreen P Amerchol

<sup>(3)</sup> Brij-98 ICI America

<sup>(4)</sup> Quadrol BASF/Wyandotte

Rather than disperse the Carbopol<sup>®</sup> resin in the water or add stock Carbopol<sup>®</sup> resin dispersion, add, with stirring, the Carbopol<sup>®</sup> resin to the alcohol (a dump-in procedure). Then add all the other actives. When these are evenly dispersed, add the water. This results in a thin, easily stirred dispersion. Add the Quadrol last to produce thickening.

This procedure minimizes air entrapment and simplifies production. This level of sunscreen usually protects the Carbopol<sup>®</sup> resins, but should unacceptable viscosity loss occur, addition of Di-sodium EDTA should be considered.

## B ating Bubbles

Sometimes bubble content in a clear gel Carbopol<sup>®</sup> resin system must be controlled to satisfy marketing goals. The goal may be zero bubbles or, again, "just the right amount" to add visual appeal. The two major sources of bubbles are from mechanical entrapment and chemical generation.

Minimize mechanical bubble formation by careful dispersion of the Carbopol<sup>®</sup> resins and by arranging for air bubble release before neutralization. In simple systems, this can be handled by allowing the dispersion to stand. In sophisticated systems, vacuum de-aeration (or even vacuum mixing) readily eliminates bubbles.

Another method to control bubble inclusion is to avoid disturbing the gel-air interface. Even slow speed mixers, that break the gel surface mechanically, incorporate air. Be certain impellers are large, low speed sweep types that are entirely submerged. Such systems should slowly turn over the gel and can de-aerate in the process.

Filling equipment must be flooded, purged of air, and kept flooded to avoid air inclusion. Look to the packings on a piston tuber, for example, to avoid air injection.

A frequent cause of bubbles, especially myriads of tiny ones, is neutralizer that has become carbonated upon exposure to air. When added to the acidic Carbopol<sup>®</sup> resin dispersion, the CO<sub>2</sub> is liberated. To avoid this, store neutralizing agents in closed containers. On a production basis, careful inventory rotation of the neutralizer can minimize the problem.

## Conclusion

Carbopol<sup>®</sup> resin products have complexities that contribute to their ultimate performance. An understanding of these complexities assures the professional chemist successful production formulation, production and performance.

Many of the listed ingredients may require special handling. It is the user's responsibility to obtain and follow the current recommendations and safety precautions of the individual additive supplier.

*Many of the listed ingredients may require special handling. It is the user's responsibility to obtain and follow the current recommendations and safety precautions of the individual additive supplier.*

# Advances in Carbomer Polymer Technology

D.D. Desai, D. F. Hasman, J. F. Schmucker-Castner, BFGoodrich, Specialty Chemicals

## Abstract

A new carbomer polymer (Carbopol® Ultrez™ 10) has been recently introduced that is easily dispersible and environmentally friendly. This new polymeric additive has a unique rigid particle structure that makes it more efficient at building viscosity. Due to this extraordinary behavior, this new polymer may be able to replace several grades of traditionally-used polymers in certain formulations.

Comparisons of fundamental and application properties among a number of different carbomers are presented to highlight the behavior differences of the Carbopol Ultrez 10 polymer. Examples of the use of this new polymer in a broad spectrum of personal care product formulations are also given.

## Introduction

Carbomer polymers have been used as rheology control or structure-building agents [1] in cosmetic lotions, creams and gels for over forty years. Over the years, personal care product manufacturers have raised concerns about the environmental safety of the solvent used in the manufacturing of carbomer polymers. The traditional Carbopol polymers are manufactured by precipitation polymerization in benzene. The BFGoodrich Company addressed these toxicological, environmental and governmental legislative concerns and, in 1992, introduced [2] a new series of carbomer polymers made in ethyl acetate-cyclohexane co-solvent as virtual replacements for traditional polymers made in benzene.

Other concerns raised by users of carbomer polymers are the difficulty in initially dispersing carbomer polymer in water and their dusty nature, with its concomitant health hazard. Both these problems were resolved by the new easy-to-disperse surfactant-modified carbomer (interpolymer) technology developed and patented [3] in 1994 by BFGoodrich researchers.

It has been the general practice of cosmetic formulators to select appropriate but different grades of carbomer polymers to thicken diverse personal care products such as lotions, creams or gels each with its own unique rheology. Quite recently The BFGoodrich Company introduced [4] Carbopol Ultrez 10 carbomer polymer, developed as the culmination of research on a safe polymerization solvent system and easy-to-disperse interpolymer carbomer technologies. Carbopol Ultrez 10 carbomer polymer is considered a universal polymer capable of replacing two or more carbomer polymer grades currently used to formulate lotions, creams or gels. Because of its universal

rheology control characteristics (i. e., use a single polymer instead of two or more carbomer grades) and, in some formulation scenarios, its higher efficiency compared to traditional carbomer polymers, substantial cost savings in the manufacture of personal care products may be realized.

We present here certain fundamental and application properties of the new Carbopol Ultrez 10 carbomer polymer in comparison to similar properties of three traditional (Carbopol 941, 940, 934) carbomer polymers. These properties illustrate the unique features of this universal carbomer polymer specially designed for formulating challenges of diverse personal care products for the 1990's and beyond. We also include here similar data for a hydrophobically modified copolymer (Carbopol® ETD™ 2020) designed for use in higher electrolyte or surfactant-containing personal care products such as shampoos.

## Fundamental Properties

### *Intrinsic Viscosity*

Carbomers are high molecular weight network polymers consisting of acrylic acid backbones and small amounts of polyalkenyl polyether crosslinking agents. Comonomers such as C10-C30 alkyl acrylates are sometimes used to hydrophobically modify homopolymer carbomers to improve their electrolyte tolerance. Water soluble or (dispersible) polymer molecules possess the unique capacity to greatly increase the viscosity of the liquid in which they are dissolved (dispersed), even when present at concentrations considered quite low. This is due to the voluminous character of the water swollen carbomer microgels [5]. The capacity of a polymer to enhance the viscosity is characterized by its "intrinsic viscosity", a structure-related parameter introduced by Staudinger [6]. The units in which intrinsic viscosity is expressed, dL/g, originate from Einstein's relationship between a polymer's specific volume and its viscosity. Factors affecting the intrinsic viscosity of a carbomer polymer include pH, electrolyte type and ionic strength, i.e., factors which also influence the molecular conformation and therefore the specific volume of the swollen polymer. The magnitude of intrinsic viscosity of a series of polymer homologs in the same background electrolyte environment, according to Staudinger, is related in a complex way to the effective molecular weight of the polymer. Intrinsic viscosities of Carbopol 941, 940, 934, Ultrez 10 and ETD-2020 carbomer polymers were determined by well known dilute solution viscometric procedures [7]. We chose a Tris®-HCl-NaCl buffer [8] electrolyte system as the background electrolyte which is representative of personal care lotions, creams and gels. This background electrolyte was prepared using Tris(hydroxymethyl)aminomethane + HCl buffer solution at pH of 7.6 with additional sodium chloride to bring the ionic strength to 0.17 or equivalent to 1.0 weight percent sodium chloride. To this was added appropriate amounts of carbomer polymer neutralized to a pH range of 7.3-8.2 using sodium hydroxide to give polymer concentrations in the range of 0-0.04 g/dL. The viscosities of these dilute polymer solutions were measured using a Physica LS-100 Low Stress rheometer. The solution viscosity ( $\eta$ ) obtained was constant (Newtonian behavior) and the relative viscosity ( $\eta/\eta_0$ ), where  $\eta_0$  is the solvent viscosity, was well within Flory's

recommendations [5]. Reduced viscosity  $((\eta/\eta_0 - 1)/c)$  vs polymer concentration (c) plots, were constructed from these data for the five polymers and are fitted by equation 1:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (1)$$

where,

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

and,  $[\eta]$  = intrinsic viscosity

The intercept at zero polymer concentration is the intrinsic viscosity listed in Table 1.

Table 1: Intrinsic Viscosity (Ionic Strength: 0.17; Tris-NaCl equal to 1.0 g/dL NaCl; pH: 7.6)		
Carbomer	$[\eta]$ .dL/g	k'
Carbopol 941	7.59	35.0
Carbopol 940	4.49	12.8
Carbopol 934	3.85	8.3
Carbopol Ultrez 10	2.60	9.9
Carbopol ETD-2020	1.89	43.6

#### *Intrinsic Volume-Swelling Ratio*

Einstein [10] showed that the viscosity of a fluid in which small rigid spheres are dilutely and uniformly dispersed, i.e., random close packing model, is related to the volume fraction occupied by all the rigid spheres. We hereby specify  $Q_i$  as the intrinsic volume-swelling ratio, which is equal to the volume of swollen polymer/volume of dry polymer, and which follows Equation 2:

$$\frac{1}{Q_i} = \frac{2.5}{100[\eta]\delta_p} \quad (2)$$

where,

$\delta_p$  = particle density, g / cm<sup>3</sup>

Table 2 gives the results of Equation 2. The particle densities of dry carbomers were determined through well-known pycnometric procedures [11] in 2,2,4 trimethyl pentane (Aldrich: 36,006-6).

Table 2: Intrinsic Volume-Swelling Ratio (Ionic Strength: 0.17; Tris-NaCl equal to 1.0 g/dL NaCl; pH: 7.6)	
Carbomer	$Q_i$
Carbopol 941	446.6
Carbopol 940	263.8
Carbopol 934	214.1
Carbopol Ultrez 10	142.2
Carbopol ETD 2020	101.5

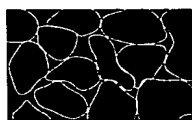
### *Overlap Concentration*

Taylor and Bagley [12] were the first to explain the extraordinary viscosity building properties of carbomer polymers even at low concentrations in terms of a two-phase microgel model. According to their model, carbomer polymer dispersions consist of swollen, deformable gel particles closely packed in intimate contact [13]. Under high dilution or at high ionic strength conditions, the gel particles no longer are tightly packed, the (interstitial) solvent is present in excess, the viscosity drops precipitously and the thickening action almost disappears. Steeneken [14] further developed this model by taking into account the existence of two concentration regimes (Figure 1a, c). In the dilute regime the dispersion is essentially nonhomogeneous and its viscosity is low and governed by the polymer volume fraction in swollen microgel. The swollen microgels are farther apart and the dispersion is either already unstable, i.e., separated into two-phases, or will become unstable over time.

**Figure 1**

(a) Dilute:

Particles are swollen to equilibrium ( $c < c^*$ )

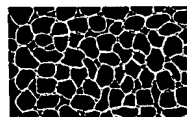


(b) Transition Regime:

Particles are swollen to equilibrium ( $c = c^*$ )

(c) Concentrated:

Particles are swollen to less than equilibrium ( $c > c^*$ )



This dilute dispersion is Newtonian and does not have yield value [15]. In the higher concentration regime the dispersion becomes homogenous and its viscosity is high

and governed by microgel particle rigidity. Here the swollen microgels are compressed, the dispersion is stable, the system is now viscoelastic and has a definite yield value. Between these two limiting cases a broad transition region exists where the viscosity is governed by both polymer volume fraction and microgel particle rigidity. At the polymer concentration at which this transition just begins, the microgels are fully swollen and just touch each other (Figure 1b). This concentration is called the "overlap concentration" ( $c^*$ ). At  $c^*$ , which is dependent on polymer type, electrolyte type and electrolyte concentration, the viscosity of the system rises sharply. Assuming Einstein's rigid sphere model, the condition that the swollen microgels do not lose any entrapped solvent, and a random close packing volume fraction ( $\phi^*$ ) of 0.637 [16], the critical overlap concentration is calculated by Equation 3:

$$c^* = \frac{100\phi^* \delta_p}{Q_i} \quad (3)$$

The resin parameters  $[\eta]$ ,  $Q_i$ , and  $c^*$  are all indicative of the thickening (or viscosity building) efficiency of a polymer in a chosen environment, i.e., solvent or background electrolyte. Thus:

Relative thickening efficiency	$[\eta]$	$Q_i$	$c^*$
High	High	High	Low
Low	Low	Low	High

Table 3 summarizes the results of Equation 3 for the five carbomer polymers under investigation.

Table 3 OVERLAP CONCENTRATION (Ionic Strength: 0.17; Tris-NaCl equal to 0.1 g/dL NaCl; pH: 7.6)	
Carbomer	$c^*$ , g/dL
Carbopol 941	0.20
Carbopol 940	0.35
Carbopol 934	0.41
Carbopol Ultrez 10	0.61
Carbopol ETD-2020	0.84

#### *Rheological Profiles*

Typical rheological profiles of 1.0 weight percent sodium hydroxide neutralized carbomer polymer mucilages (pH: 7.3-8.2) were determined using a Physica UM-MC 100 controlled stress rheometer. Internally standardized sample preparation and test protocols were used and the following rheological parameters were determined for the

five carbomer polymers under investigation. The rheological parameters, what each parameter signifies, and quantitative values of each parameter are given in Table 4.

Table 4 RHEOLOGICAL PROFILES (1.0 wt % NaOH neutralized carbomer mucilages; pH: 7.3-8.2; 25°C)					
Rheology Parameter	C-941	C-940	C-934	Ultrez 10	ETD-2020
$G^0$ , Pa	25.5	425.0	736.9	983.3	325.8
T. I., Pa/s·cm <sup>3</sup>	4.6	42.9	304.9	309.0	11.5
$\tau_{yld}$ , Pa	13.5	98.5	94.5	108.1	147.2
$\eta\#$ , mPa·s	10,700	75,800	74,500	84,300	63,200
(# measured at 2.041 s <sup>-1</sup> )					

$G^0$	:	RIGIDITY COEFFICIENT, Pa - A larger value denotes more particle behavior of the polymer and a more rigid gel.
T.I.	:	THIXOTROPIC INDEX, Pa/s cm <sup>3</sup> - A larger value denotes more particle behavior, lower gel-strength, larger swollen microgel particle size and more cloudy mucilage.
$\tau_{yld}$	:	YIELD POINT, Pa - A larger value denotes better suspension/emulsion stability.
$\eta @ 2.041 \text{ s}^{-1}$	:	Viscosity, mPa.s at 2.041 s <sup>-1</sup> , equivalent to Brookfield Spindle No. 7 at 20 rpm.

Using highly sensitive and modern rheometers, the quantitative values of rheological parameters vary depending on sample preparation and the test protocols used. Therefore, the results listed in Table 5 have more value when looked at collectively rather than the individual numbers themselves.

#### Unique Fundamental Features Of Ultrez-10 Carbomer Polymer

Carbomer polymer is a special case of nonlinear, branched polymer chains which interconnect to form a 3-dimensional network structure. In dispersions consisting of network polymers the dominant structural feature is (water) swollen microgels. Polymer microgel particles increase the viscosity of a solution essentially through two mechanisms:



- (i) At concentrations lower than the overlap concentration, viscosity increases in direct proportion to the magnitude of polymer swelling. In this region carbomer polymers with low crosslink density which produce soft (low rigidity), compressible microgels, high intrinsic viscosity and high intrinsic swellability are the preferred carbomer polymers (e.g. C-941, C-940) for efficient viscosity building.
- (ii) On the other hand, above overlap concentration, the governing factor in viscosity building is the microgel rigidity. High crosslink density carbomer polymers (e.g., C-934) which produce particle-like harder microgels contribute significantly to their viscosity building performance. Here, viscosity of the system increases in direct proportion to microgel particle rigidity.

It is interesting to note here that both high crosslink density and high microgel rigidity, as in Carbopol Ultrez 10, yield the most efficient carbomer polymers for viscosity building. The ETD-2020 carbomer polymer, though it has a high crosslink density, is less efficient than Carbopol Ultrez 10 (at ionic strength: 0.17) because of its lower rigidity (see Table 4) in comparison to Carbopol Ultrez 10. At considerably higher ionic strengths, ETD-2020 carbomer polymer can be expected to outperform other carbomer polymers since it is hydrophobically modified to provide better electrolyte tolerance.

Because of the dual nature of viscosity building by carbomer polymers, an interesting crossover phenomenon occurs. Low swelling carbomer polymers (e.g. Carbopol Ultrez 10, C-934) have a lower viscosity at low polymer concentration; however, at higher polymer concentrations this situation is reversed. This illustrates the unique rigid particle nature of Carbopol Ultrez 10 resin as compared to traditional C-940 and C-934 resins. In fact, the fundamental data given in this paper show that the new Carbopol Ultrez-10 carbomer polymer is capable of replacing either C-940 or C-934 in certain personal care product formulations.

### **Application Properties Of Personal Care Products With Ultrez 10 Polymer**

Some of the unique features of Carbopol Ultrez 10 carbomer polymer in real-life personal care product processing and formulating situations are discussed below and, wherever possible, explained in relation to the appropriate fundamental polymer structure or mucilage properties mentioned in the earlier sections of this paper.

#### **Ease Of Dispersion**

Significant time and money can be saved by using Carbopol Ultrez 10 carbomer polymer as compared to traditional carbomer polymers or even the newly introduced easy-to-disperse surfactant-modified interpolymer [3] such as Carbopol ETD-2020 carbomer polymer. To support this claim, we present here wetting time data for the five carbomer polymers under discussion (Table 5). The wetting time is determined as

follows: Dry 2.5 grams of Carbopol carbomer polymer in a vacuum oven at 80°C and 0.97 atm of Hg for 1 hour. Sprinkle or dump the polymer, at one time, onto the surface of 500 mL of demineralized water contained in a beaker. Start a timer as you dump the polymer. The Carbopol Ultrez 10 carbomer polymer will begin to wet in seconds and incorporate into water. Note the time when the dry powder is no longer visible either on the surface or the bulk of water in the beaker. This is the wetting time. The shorter the wetting time the easier it is to disperse the carbomer polymer in water. At this time a minimum of agitation or stirring will produce a lump free carbomer dispersion.

The significant reduction in wetting time for Carbopol Ultrez 10, and to a lesser extent for Carbopol ETD-2020, is the result of both the surface active nature of these interpolymers, and, in the case of Carbopol Ultrez 10 carbomer polymer, the increased particle-like behavior as opposed to swelling only.

Table 5: Wetting Times During Initial Dispersion Stage	
Carbomer	Wetting Time, min
C-941	>>50
C-940	>50
C-934	>50
Ultrez 10	5
ETD-2020	15

#### Low Dispersion Viscosity

One of the unusual features of Carbopol Ultrez 10 carbomer polymer is the low (unneutralized carbomer polymer) dispersion viscosity, unlike the high dispersion viscosities of traditional carbomer polymers. Table 6 illustrates this unique aspect of Carbopol Ultrez 10 carbomer polymer.

Table 6 Viscosity Of Unneutralized Aqueous Carbomer Polymer Dispersions (Brookfield Viscometer; 20 rpm; pH: 2.5-3.5; 23°C)						
Carbomer - Wt. % Concentration of the Resin	Viscosity, mPa.s(cP)					
	0.5	1.0	2.0	3.0	4.0	5.0
C-941	2,970	4,630	5,560	6,980	16,450	26,950
C-940	680	4,150	10,580	26,350	57,600	82,400
C-934	17	105	2,820	7,260	19,750	32,700
Ultrez 10	7	9	41	164	1,130	4,500
ETD-2020	17	108	740	3,410	7,010	19,250

The low dispersion viscosity of aqueous Carbopol Ultrez 10 polymer dispersions enables the following important processing and/or cost saving advantages:

- (i) Unlike the traditional carbomer polymers, it is possible to prepare very concentrated dispersion stock solutions with Carbopol Ultrez 10 polymer. When a master batch is needed, a single batch at a concentration even as high as 5 % can be made more easily and more rapidly, saving valuable production time.
- (ii) If the master batch of unneutralized carbomer polymer stock dispersion needs to be pumped and transported along pipe lines within the production site, the low viscosity of Carbopol Ultrez 10 polymer dispersions makes this easier to accomplish.
- (iii) Because of the low viscosity of concentrated Carbopol Ultrez 10 carbomer polymer stock dispersions, less foam is created during the initial stages of mixing due to less entrapment of air. Also, for the same reason, the subsequent mixing of additional ingredients is easy, reducing the processing time. The low dispersion viscosity at high concentrations of Carbopol Ultrez 10 carbomer polymer dispersions is primarily due to enhanced particle behavior of the resin. We reiterate here that Carbopol Ultrez 10 resin thickens systems principally because of its higher rigidity rather than its swelling behavior. In traditional carbomer polymer dispersions the situation is exactly the reverse and hence the higher viscosities of their dispersions.

#### **Single Polymer For Broad Spectrum Of Personal Care Applications**

Because of the unique balance between the swelling and the particle-like behavior in Carbopol Ultrez 10 carbomer polymer, it is now possible for a personal care formulator to create everything from thin lotions to thicker creams using only a single rheology modifier. Examples 1 to 3 illustrate this one-polymer-for-a-broad-spectrum-of-applications concept. Current practice in the personal care industry is to use different carbomer polymers for lotions, creams and gels depending on the desired final viscosity of the product.

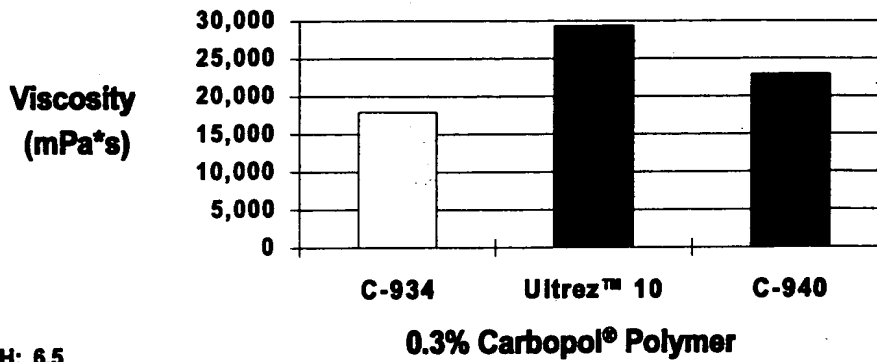
#### **Enhanced Performance Benefits**

##### *(i) Cost-Efficiency:*

The dual nature of viscosity building by the new Carbopol Ultrez 10 carbomer polymer, i.e., thickening by swelling at concentrations close to its overlap concentration, and, thickening by its rigid particle nature at higher concentrations, leads to some interesting cost-efficiency considerations. It has been observed, for example, that certain personal care product formulations prepared with Carbopol Ultrez 10 carbomer polymer have 10, 20 or even 40 % more viscosity than those prepared with traditional carbomer polymers like Carbopol 934, at the same thickener levels; Example 1 includes a bar graph showing this benefit. Or, conversely, significantly less carbomer polymer level in the

formulation is required for Carbopol Ultrez 10 carbomer polymer as compared to traditional carbomer polymers to reach the same final viscosity in the product.

**Example 1:**  
**Efficiency of Carbopol® Ultrez™ 10 in Hand & Body Lotion**



**pH: 6.5**

**Viscosity: Brookfield RVT @ 20 rpm, #6 spindle**

**(ii) Less Tacky Feel:**

The new Carbopol Ultrez 10 carbomer polymer swells significantly less than the traditional carbomer polymers (see Table 2) and its thixotropic index is generally higher than those of traditional carbomer polymers. This unique combination of fundamental properties results in less tackiness of personal care products formulated with Carbopol Ultrez 10 carbomer polymer as compared with products thickened with traditional carbomer polymers. This improved, less tacky, feel has in fact been observed consistently in all formulations prepared in our laboratory with Carbopol Ultrez 10 carbomer polymer and corroborated by some BFGoodrich customers as well.

**Conclusion**

Carbopol Ultrez 10 carbomer polymer is shown to be a universal polymer in that it can replace two or more grades of carbomer polymer in certain personal care product formulations. Carbopol Ultrez 10 carbomer polymer has a unique rigid particle structure that makes it more efficient at building viscosity. This efficiency is identified to be due to this carbomer polymer having both high crosslink density and high microgel rigidity. Carbopol Ultrez 10 carbomer polymer disperses more quickly than other carbomer polymers due to its surface activity as well as its display of more particle-like behavior. This particle-like behavior leads to lower dispersion viscosity and less microgel swelling. The lower swelling of Carbopol Ultrez 10 carbomer polymer, when combined with a greater thixotropic index, gives certain personal care products a less tacky feel than those obtained with traditional carbomer polymers.

## Acknowledgment

The authors wish to thank the BFGoodrich Company for permission to publish this paper.

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### Example 1

#### Hand And Body Lotion

This hand and body lotion combines skin moisturizing and protective properties with a non-tacky, natural skin feel. (Bar graph shows viscosity efficiency of Carbopol Ultrez 10 in this formulation.)

<b>Ingredient/CTFA-INCI Name</b>	<b>Weight %</b>	<b>Function</b>
<b>PART A</b>		
Deionized Water	83.90	Diluent
Disodium EDTA	0.10	Chelating Agent
Carbomer*	0.20	Thickening Agent
<b>PART B</b>		
Propylene Glycol	0.80	Humectant
Glycerin	5.00	Humectant
Methylparaben	0.20	Preservative
Propylparaben	0.10	Preservative
<b>PART C</b>		
Mineral Oil	4.00	Moisture Barrier
Stearic Acid (triple pressed)	2.00	Moisture Barrier
Glycol Stearate	1.50	Opacifier
Cetyl Acetate/Acetylated	0.50	Moisture Barrier
Lanolin Alcohol		
Glyceryl Stearate	0.50	Emulsifier
Cetyl Alcohol	0.20	Moisture Barrier
Dimethicone	0.50	Lubricant
<b>PART D</b>		
Triethanolamine (99%)	0.50	Neutralizing Agent
*Carbopol® Ultrez™ 10		

#### Properties

pH:	6.9 - 7.3
Viscosity** (mPa.s):	14,000 - 20,000
Color, odor, appearance:	Thick, white, glossy emulsion

\*\*Brookfield RVT @ 20 rpm, 25°C, #5 spindle

#### Preparation Procedure

1. Add disodium EDTA to the water. Mix until dissolved.
2. Disperse Carbopol® Ultrez™ 10 in the water. After resin has fully wetted, mix at a slow speed.
3. Combine PART B. Heat slightly and mix until the parabens are dissolved. Add to PART A.
4. Heat the combined PARTS A and B to 65°C.
5. Combine PART C. Heat to 65°C and mix slightly until all the solids are dissolved.
6. Add PART C to PARTS A and B. While the temperature is at 65°C, add PART D.
7. Mix the emulsion with moderate agitation until the temperature reaches 40°C. Cool to room temperature.

## Example 2

### Hair Styling Cream With Natural Oils And Conditioners

This styling cream contains natural oils to provide moisturization and shine. This light emulsion can be used to style and define hair without leaving a heavy greasy feel. This formula also contains cationic conditioners to provide excellent static control and feel, and a sunscreen to protect the hair from UV damage.

Ingredient/CTFA-INCI Name	Weight %	Function
<b>PART A</b>		
Meadowfoam Seed Oil	3.00	Moisturizer
Apricot Kernel Oil	3.00	Moisturizer
Phenyl Trimethicone	2.00	Shine Enhancer
C12-15 Alkyl Benzoate	2.00	Emollient
Glyceryl Stearate	2.00	Bodifying Agent
Octyl Methoxycinnamate	4.00	UV Absorber
Tocopheryl Acetate	0.50	Antioxidant/Free Radical Scavenger
Acrylates/ C10-30 Alkyl Acrylate Crosspolymer*	0.25	Emulsifier
Carbomer**	0.15	Thickener
* Pemulen® TR-1** Carbopol® Ultrez™ 10		
<b>PART B</b>		
Deionized Water	78.92	Diluent
PVP (100%)	1.00	Hair Setting Agent
Triethanolamine (99%)	0.38	Neutralizer
<b>PART C</b>		
PEG-20 Almond Glycerides	0.20	Particle Size Reducer
Linoleamidopropyl PG-Dimonium Chloride Phosphate	0.30	Hair Conditioner
Cocodimonium Hydroxylpropyl Hydrolyzed Wheat Protein	0.30	Hair Conditioner
Fruity Floral Fragrance	1.00	Fragrance
Propylene Glycol (and) Methylparaben (and) Propylparaben (and) Diazolidinyl Urea	1.00	Preservative

### *Example 2 (continued)*

#### **Properties**

Color, odor, appearance:	Thick, glossy, creamy emulsion
pH:	6.0 - 6.8
Viscosity*** (mPa·s) at 25°C:	20,000 - 40,000

\*\*\*Brookfield RVT @ 20 rpm, #6 spindle

#### **Preparation procedure**

1. PART A: Combine all oil phase ingredients, heat mixture to 60 - 65°C, mix until uniform. Disperse Pemulen® TR-1 and Carbopol® Ultrez™ 10 polymers in oil phase. Mix until powders are dispersed well.
2. PART B: Disperse PVP K-90 in deionized water (55 - 60°C). Mix until polymer is hydrated. Add triethanolamine to solution.
3. Add PART A to PART B. Both phases should be at 55 - 60°C. Mix until no lumps remain and batch is uniform, maintaining a temperature of 55 - 60°C.
4. PART C: Add Crovol A-40 to batch. NOTE: Batch may invert to a water in oil emulsion (batch will look curdled). Keep mixing and cool batch to 40 - 45°C. Keep mixing until batch reinverts to an oil-in-water emulsion (extra shear agitation may be necessary if the batch has still not reinverted at 40°C).
5. PART C: After the batch has cooled to 40 - 45°C and inversion is complete, add the remaining PART C ingredients. Mix until uniform.



### Example 3

#### Icy Blue Camphorated Gel

This brilliant clear blue camphorated gel demonstrates the use of Carbopol® Ultrez™ 10.

<b>Ingredient /CTFA-INCI Name</b>	<b>Weight, %</b>	<b>Function</b>
<b>PART A</b>		
Deionized Water	86.06	Diluent
Disodium EDTA	0.10	Chelating Agent
<b>Carbomer*</b>	0.90	Thickener
<b>PART B</b>		
Isopropyl Alcohol	10.00	Solvent
Camphor (Crystals)	0.20	Active
Polysorbate 20	1.00	Surfactant
Triethanolamine (99%)	1.50	Neutralizer
Methylparaben	0.20	Preservative
FD&C Blue No. 1 (5% solution)	0.04	Dye
<b>*Carbopol® Ultrez™ 10</b>		

#### Properties

pH	7.2 - 7.6
Viscosity**(mPa·s)	40,000 - 48,000

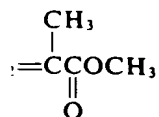
\*\*Brookfield RVT @ 20 rpm, #6 spindle

#### Preparation Procedure

1. PART A: Dissolve disodium EDTA in warm deionized water (25 - 45°C). Slowly sprinkle Carbopol® Ultrez™ 10 on the surface of deionized water. After the polymer is thoroughly wetted, mix at a slow speed.
2. Separately combine PART B. Add to PART A with moderate sweeping agitation until a clear gel is formed.

## -CHAIN POLYMERS

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omotive lenses, re-  
ipment, and home

## ACRYLIC POLYMERS

389

furnishings. Acrylic sheeting is used for signs, glazing (in particular, aircraft win-  
dows), furniture, partitions, and lighting-fixture diffusers. About 0.5 billion lb of  
acrylic plastics was sold in 1982.

Copolymers of methyl methacrylate, ethyl acrylate, and monomers containing  
reactive functional groups are widely used as thermosetting resins in baked enamel  
applications. The functionality can be derived from amides (acrylamide, methacryla-  
mide), acids (acrylic acid, methacrylic acid, or others), hydroxyls (hydroxyalkyl  
acrylates or methacrylates), or oxiranes (glycidyl methacrylate).

## Other Acrylic Plastics

**Higher Methacrylates.** The monomers of higher alkyl methacrylates are most  
conveniently prepared from methyl methacrylate by alcoholysis. The reaction is  
carried out at 150°C with an excess of the alcohol whose methacrylate ester is  
desired and a small amount of sulfuric acid catalyst. As described in Chapter 12B,  
the higher alkyl methacrylate polymers have glass transition temperatures lower  
than that of poly(methyl methacrylate). Poly(lauryl methacrylate) is widely used as  
a pour-point depressant and improver of viscosity-temperature characteristics for  
lubricating oils.

**Polyacrylates.** The rubbery, adhesive nature of the lower acrylates makes both  
suspension polymerization and casting less feasible than with the methacrylates.  
Consequently, solution and emulsion polymerizations are used commercially. Since  
the polyacrylates contain an easily removed tertiary hydrogen atom, they undergo  
some chain transfer to polymer when polymerized to high conversion. This leads  
to highly branched, less soluble materials.

Since the lower acrylate polymers have glass transition points below room tem-  
perature, they are typically soft and rubbery. As the size of the ester group decreases,  
the polymers become harder, tougher, and more rigid. The polyacrylates have been  
used in finishes, in textile sizes, and in the manufacture of pressure-sensitive adhesives.

Copolymers of ethyl acrylate with methyl methacrylate (to provide hardness and  
strength) and small amounts of hydroxyl, carboxyl, amine, or amide comonomers  
(to provide adhesion and thermosetting capability) are used to produce high-quality  
latex paints for wood, wallboard, and masonry in homes. Other copolymers are  
used for automotive and appliance coatings and a variety of specialty coatings,  
finishes, polishes, and adhesives.

Copolymers of ethyl acrylate with a few per cent of a chlorine-containing mon-  
omer such as 2-chloroethyl vinyl ether have elastomeric properties. Vulcanization  
reactions apparently involve the chlorine atom, ester group, and  $\alpha$ -hydrogens on  
the chain. Numerous rubber vulcanization agents and accelerators vulcanize these  
polymers. They are of interest because of their heat resistance and their excellent  
resistance to oxidation, allowing their use to over 180°C.

**Poly(acrylic acid) and Poly(methacrylic acid).** Acrylic acid,  $\text{CH}_2=\text{CHCOOH}$ ,  
can be prepared directly from ethylene cyanohydrin. Methacrylic acid can be pre-  
pared from acetone cyanohydrin. Salts of the acids can be polymerized directly,

then acidified to give poly(acrylic acid) and poly(methacrylic acid). Alternatively, poly(methyl acrylate) or poly(methyl methacrylate) may be saponified to form the acids. Or polymethacrylonitrile may be treated with hydrogen chloride to give poly(methacrylic acid). The polymers are insoluble in their monomers and in most organic liquids, but are soluble in water and very soluble in dilute bases. Poly(acrylic acid) and poly(methacrylic acid) are too water sensitive to serve as plastics. They ~~and on heating do not become thermoplastic but crosslink, and decompose.~~ In solution they show typical polyelectrolyte behavior, including abnormally high viscosities. Because of this property they are useful as thickening agents for latices and for adhesives.

**Cyanoacrylate Adhesives.** Methyl cyanoacrylate monomer is an extremely powerful adhesive. Adhesion occurs when the liquid monomer is spread in a thin layer between the surfaces to be bonded. Traces of bases (even as weak as alcohols or water) on the surfaces catalyze polymerization by an anionic mechanism. Adhesion arises in part from mechanical interlocking between polymer and surface, and in part from strong secondary bond forces.

**Polyacrylamide.** This water-soluble polymer is used as a thickening agent and as a flocculant.

#### Acrylic Fibers

The *acrylic* fibers are polymers containing at least 85% acrylonitrile. Other monomers are often used in small amount to make the polymer amenable to dyeing with conventional textile dyes. Common comonomers are vinyl acetate, acrylic esters, and vinyl pyrrolidone. The last may be used as the homopolymer in a blend or grafted onto a copolymer backbone. A generic class of fibers closely related to the acrylics is the *modacrylic* fibers, containing 35–85% acrylonitrile and, usually, 20% or more vinyl chloride or vinylidene chloride.

**Polyacrylonitrile.** Acrylonitrile can be made either by the direct catalytic addition of HCN to acetylene, or by the addition of HCN to ethylene oxide to give ethylene cyanohydrin, followed by dehydration. The monomer is soluble in water to the extent of about 7.5% at room temperature, and polymerization is usually carried out in aqueous solution by means of redox initiation. The polymer precipitates from the system as a fine powder.

During the time that other vinyl polymers were being developed commercially as plastics as well as fibers, polyacrylonitrile was considered a useless material because it could not be dissolved or plasticized. It softens only slightly below its decomposition temperature, and, because the polymer is insoluble in the monomer, it could not be polymerized into useful shapes by casting. This intractability was for a time attributed to crosslinking, but better knowledge of the requirements for solubility of polymers led to an extensive search (Houtz 1950) for molecules that might interact with the highly polar  $\text{—C}\equiv\text{N}$  groups and cause solution of the polymer. Several such solvents were discovered, among them dimethyl formamide

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# TEXTBOOK OF POLYMER SCIENCE

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THIRD EDITION

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Rensselaer Polytechnic Institute, Troy, New York*

A Wiley-Interscience Publication

John Wiley & Sons

New York • Chichester • Brisbane • Toronto • Singapore

## PREFACE

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### **Library of Congress Cataloging in Publication Data:**

Billmeyer, Fred W.

Textbook of polymer science.

Includes bibliographies and indexes.

1. Polymers and polymerization. I. Title.

QD381.B52 1984 668.9 83-19870  
ISBN 0-471-03196-8

Printed in the United States of America

10 9 8 7 6 5